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O'CONNOR, P. et al.

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Title: USE OF CATIONIC LAYERED MATERIALS,
COMPOSITIONS COMPRISING THESE
MATERIALS, AND THE PREPARATION OF
CATIONIC LAYERED MATERIALS

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Sir:

Enclosed herewith is a certified copy of European Patent Application No. 02078429.4 to support the claim of foreign priority benefits under 35 U.S.C. §119 in connection with the above-identified application.

Respectfully submitted,

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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
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Process for the preparation of catonic layered materials and compositions
comprising these materials

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D. Levin, S. Soled and J. Ying (*Chem. Mater.* Vol. 8, 1996, pp.836-843; *ACS Symp. Ser.* Vol. 622, 1996, pp. 237-249; *Stud. Surf, Sci. Catal.* Vol. 118, 1998, pp. 359-367) also disclose the preparation of CLMs. They start from an anionic clay. As already mentioned, these materials have a crystal structure which consists of positively charged layers built up of specific combinations of Me(II)-Al hydroxides with anions and water molecules in the interlayers. According to these publications, volatile or decomposable anions can be removed from the anionic clay, resulting in a mixed oxide phase. Upon contacting this mixed oxide with ammonium heptamolybdate, aluminium ions are removed and molybdate ions incorporated, resulting in a CLM with a trace amount, e.g. 0.63 wt%, of aluminium present. The anionic clay starting material according to this teaching was obtained by precipitation of water-soluble metal salts, e.g. aluminium nitrate and divalent metal nitrates.

The prior art processes for preparing CLMs thus all use water-soluble metal salts as starting material. The use of soluble metal salts for this process has several disadvantages: it is relatively expensive and washing and filtering steps are required during the preparation process to remove unwanted anions. With the fine-particled materials obtained, filtration problems can arise. Furthermore, drying or calcining the so-prepared CLMs or their intermediates can result in gaseous emissions of nitrogen oxides, halogens, sulfur oxides, etc., which will cause environmental pollution problems.

The present invention provides a process for the production of cationic layered materials using inexpensive raw materials. In particular, the use of metal salts may be avoided, resulting a process which is particularly environmentally friendly and more suited to the environmental constraints which are increasingly imposed on commercial operations. In addition, in one embodiment of this invention the formation of an anionic clay as intermediate is essentially avoided.

PROCESS FOR THE PREPARATION OF CATIONIC LAYERED MATERIALS
AND COMPOSITIONS COMPRISING THESE MATERIALS

- 5 This invention relates to a process for the preparation of cationic layered materials and compositions comprising these materials.

A Cationic Layered Material (CLM) is a crystalline $\text{NH}_4\text{-Me(II)-TM-O}$ phase with a characteristic X-ray diffraction pattern. In this structure, Me(II) represents a
10 divalent metal and TM stands for a transition metal. The structure of a CLM consists of negatively charged layers of divalent metal octahedra and transition metal tetrahedra with charge-compensating cations sandwiched between these layers.

- 15 The CLM structure is related to that of hydrotalcite and hydrotalcite-like materials. These materials, also referred to by the skilled person as layered double hydroxides (LDH) or anionic clays, are built up of Me(II)-Al hydroxide sheets with exchangeable anions in the interlayers. Analogous to the term "anionic clay" being a synonym for hydrotalcites and hydrotalcite-like materials,
20 "cationic clay" can be used as a synonym for CLM.

CLMs are known from the prior art. M.P. Astier et al. (*Ann. Chim. Fr.* Vol. 12, 1987, pp. 337-343) prepare CLMs by first dissolving ammonium heptamolybdate and nickel nitrate in an aqueous ammonia solution, and
25 subsequently altering the pH by evaporating ammonia, resulting in precipitation. After ageing, washing, and drying, pure crystalline CLMs are formed with a characteristic X-ray diffraction pattern.

A similar precipitation procedure is disclosed in US 6,156,695 for the preparation of CLMs containing Ni, W and Mo.

The process comprises the steps of:

- a) preparing a slurry comprising a water-insoluble aluminium source and a divalent metal source,
- b) drying the slurry and calcining the dried material to form a first calcined material,
- 5 c) optionally rehydrating the product of step b) to obtain an anionic clay, followed by calcining the anionic clay to form a second calcined material,
- d) contacting a slurry of either the first or the second calcined material with an ammonium transition metal salt,
- 10 e) ageing the resulting slurry.

By the term comprising is meant that the process according to the invention can include additional steps, for instance an intermediate drying step, a shaping step, a milling step, an additional ageing step, an additional calcination step, or washing and filtering steps. Moreover, additional compounds like acids, bases, 15 or metal compounds can be added where appropriate.

In a first embodiment step c) is not performed, meaning that the product of step b) is contacted with the ammonium transition metal salt, i.e. step d). In this 20 embodiment anionic clay is not formed as an intermediate, although a small amount might be formed during step (a).

In a second embodiment anionic clay is formed as intermediate product by rehydrating the material resulting from step b).

25 During ageing step e), aluminium is removed from the intermediate material. If the material is filtered and washed after step e) and if the ageing conditions are such that the removed aluminium will not become insoluble, this aluminium will not end up in the final product. However, if no washing step is applied and/or if insoluble aluminium compounds are formed during ageing, aluminium will end 30 up in the final composition as a separate aluminium-containing compound, such

as an aluminium oxide or hydroxide, a metal aluminate, or aluminium molybdate. As will be explained below, the presence of this separate aluminium-containing compound may have several advantages. The invention, therefore, also relates to compositions comprising CLM and aluminium oxide or hydroxide, metal aluminate, or aluminium molybdate.

Water-insoluble aluminium source

The water-insoluble aluminium source that can be used in the process according to the invention includes aluminium oxides and hydroxides, such as gel alumina, boehmite, pseudoboehmite (either peptised or not), aluminium trihydrates, thermally treated aluminium trihydrates, and mixtures thereof. Examples of aluminium trihydrates are crystalline aluminium trihydrate (ATH), for example gibbsite provided by Reynolds Aluminium Company RH-20® or JM Huber Micral® grades, BOC (Bauxite Ore Concentrate), bayerite, and nordstrandite. BOC is the cheapest water-insoluble aluminium source.

The water-insoluble aluminium source preferably has a small particle size, preferably below 10 microns.

Calcined aluminium trihydrate is readily obtained by thermally treating aluminium trihydrate (gibbsite) at a temperature ranging from 100° to 1,000°C for 15 minutes to 24 hours. In any event, the calcining temperature and the time for obtaining calcined aluminium trihydrate should be sufficient to cause a measurable increase of the surface area compared to the surface area of the gibbsite as produced by the Bayer process, which is generally between 30 and 50 m²/g. Within the context of this invention flash calcined alumina (e.g. Alcoa CP® alumina) is also considered to be a thermally treated form of aluminium trihydrate. Flash calcined alumina is obtained by treating aluminium trihydrate at temperatures between 800° and 1,000°C for very short periods of time in special industrial equipment, as is described in US 4,051,072 and US 3,222,129.

The water-insoluble aluminium source may have been doped with metal compounds, for instance rare earth metals or transition metals. Examples are compounds of, for instance, Ce, La, V, Mg, Ni, Mo, W, Mn, Fe, Nb, Ga, Si, P, Bi, B, Ti, Zr, Cr, Zn, Cu, Co, and combinations thereof, preferably in amounts
5 between 1 and 40 wt%. The desired metal depends on the application of the final product. For example, for hydroprocessing applications Mo, Co, Ni, W are preferred, while for FCC applications preference is given to V, Ce, La, Ni, Zn, Fe, Cu, W, Mo. This doped water-insoluble aluminium source can be obtained by any method known in the art, for instance thermal or hydrothermal treatment
10 of the water-insoluble aluminium source with the metal compound. Preferably oxides, hydroxides, and carbonates of the metals are used, but also nitrates, chlorides, sulfates, phosphates, acetates and oxalates can be used. When a doped water-insoluble aluminium source is used as a starting material for the preparation of compositions comprising CLM and aluminium oxide or hydroxide,
15 doped aluminium oxide or hydroxide (in a controlled amount) will be present in the final product. This may be beneficial for several applications.

Divalent metal source

Suitable divalent metal sources to be used in the process according to the
20 invention are compounds containing Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Fe^{2+} , Ca^{2+} , Ba^{2+} , and mixtures of said compounds. Both solid divalent metal sources and soluble divalent metal sources (e.g. nitrates, chlorides, acetates, etc.) are suitable. Preferably oxides, hydroxides, carbonates, hydroxycarbonates, formates, or acetates are used. Combinations of divalent metal sources may be
25 used as well.

The divalent metal source may have been doped with metals, such as Al, Ga, Cr, Fe, V, B, In, Nb, W, Mo, Ta, or mixtures thereof. This doped divalent metal source can be obtained by any method known in the art, for instance thermal or
30 hydrothermal treatment of the divalent metal source with the metal compound.

Preferably oxides, hydroxides, and carbonates of the metals are used, but also nitrates, chlorides, sulfates, phosphates, acetates, and oxalates can be used.

Ammonium transition metal salt

- 5 Suitable ammonium transition metal salts include ammonium heptamolybdate, ammonium tungstate, ammonium vanadate, ammonium dichromate, ammonium borate, ammonium phosphate, ammonium titanate, and ammonium zirconate. Combinations of these compounds may also be used.

10 Process conditions

The process according to the invention can be conducted in either batch or continuous mode, optionally in a continuous multi-step operation. The process can also be conducted partly batch-wise and partly continuous.

- 15 The water-insoluble aluminium source and the divalent metal source are added to a reactor and slurried in water. The reactor can be heated by any heating source such as a furnace, microwave, infrared sources, heating jackets (either electrical or with a heating fluid), lamps, etc. The reactor may be equipped with stirrers, baffles, etc., to ensure homogeneous mixing of the reactants.

- 20 The aqueous suspension in the reactor may be obtained by combining water, the divalent metal source, and the water-insoluble aluminium source either *per se*, as slurries, or combinations thereof. Additionally, in the case of a water-soluble divalent metal source, the divalent metal source can be added as a solution. Any sequence of addition can be used: the divalent metal source can be added to a slurry of the water-insoluble aluminium source, the water-insoluble aluminium source can be added to a slurry or solution of the divalent metal source, or both the water-insoluble aluminium source and the divalent metal source can be added to the reactor at the same time.

- 25 Optionally, the resulting mixture and/or the separate sources are homogenised by, for instance, milling, high shear mixing or kneading. Especially when using metal sources like oxides, hydroxides or carbonates, it is usually advisable to
- 30

mill the metal sources. Preferably, both the water-insoluble aluminium source and the divalent metal source - if water-insoluble - are milled. Even more preferably, a slurry comprising both the water-insoluble aluminium source and the divalent metal source is milled.

5

If desired, organic or inorganic acids and bases, for example for control of the pH, may be fed to the reactor or added to either the divalent metal source or the water-insoluble aluminium source before they are fed to the reactor. A preferred pH modifier is an ammonium base, because upon drying no deleterious cations remain in the product.

10

Optionally, the mixture can be aged after step a). This ageing can be performed under, or close to, ambient conditions, or under thermal or hydrothermal conditions. Within the context of this description hydrothermal means in the presence of water (or steam) at a temperature above 100°C at elevated pressure, e.g. autogenous pressure. The ageing temperature can range from 20°-400°C. A preferred temperature range is 60-175°C. Suitable atmospheres comprise CO₂, N₂, and air. The preferred atmosphere is air.

15

With this ageing step it is possible, for instance, to convert the aluminium source into another aluminium source with improved binding properties. For instance, it is possible to convert aluminium trihydrate into boehmite.

20

The calcination according to step b) is conducted at temperatures between 175° and 1,000°C, preferably between 200° and 800°C, more preferably between 400° and 500°C, and most preferably around 400°C. This calcination is conducted for 15 minutes to 24 hours, preferably 1-12 hours, and most preferably 2-6 hours. The resulting material will be referred to as the first calcined material.

25

In the process according to the second embodiment of this invention, the first calcined material, after an optional milling step, is rehydrated in aqueous suspension to obtain an anionic clay. This rehydration can be performed at thermal or hydrothermal conditions and in the presence of dissolved metal salts, such salts including nitrates, carbonates, sulphates, oxalates of divalent (e.g. Zn, Mn, Co, Ni, Cu) or trivalent metals (e.g. Ga, Cr, Fe, V, Mo, W).

If rehydration is performed, the obtained anionic clay is subsequently calcined to obtain a second calcined material. This second calcination is performed at temperatures between 150° and 1,000°C, preferably between 200° and 800°C, more preferably between 200° and 600°C, and most preferably around 400°C. This calcination is conducted for 15 minutes to 24 hours, preferably 1-12 hours, and most preferably 2-6 hours.

A slurry of either the first (cf. the first embodiment) or the second calcined material (cf. the second embodiment) is subsequently contacted with an ammonium transition metal salt. To this end, a slurry of the calcined material, after an optional milling step, is added to a slurry or solution of the metal salt, or *vice versa*. It is also possible to treat the slurry of the calcined material at elevated temperature and then add the ammonium transition metal salt *per se*, or as a slurry or solution. Alternatively, the ammonium transition metal salt slurry or solution can be prepared by adding another transition metal compound, e.g. an oxide or hydroxide, to aqueous ammonia. If aqueous ammonia is present in the reactor, this slurry or solution can be prepared *in situ* by feeding the transition metal compound, as a solid, solution or slurry, to the reactor.

The slurry is aged at temperatures of 20°-300°C, preferably 60°-200°C, for 15 minutes to 24 hours, preferably 1-12 hours, more preferably 2-6 hours, with or without stirring, at ambient or elevated temperature and at atmospheric or elevated pressure. Suitable atmospheres comprise CO₂, N₂, or air. The

preferred atmosphere is air.

During this ageing step, aluminium is removed from the material as dissolved species. A washing and filtering step may optionally be performed in order to prevent at least a portion of the aluminium from becoming part of the resulting product. The so-formed product will comprise predominantly CLM with an X-ray diffraction pattern analogous to the aforementioned CLMs obtained by Astier et al. By predominantly CLM is meant that the product will comprise more than 50 percent and preferably more than 70% CLM.

Compositions comprising CLM and an aluminium-containing compound are obtained if no washing and filtering step is performed and/or if insoluble aluminium compounds are formed during ageing by changing the ageing conditions, e.g. increasing the pH and/or the temperature. The types of aluminium-containing compounds will depend on the ageing conditions. Examples of such aluminium-containing compounds are aluminium oxides, hydroxides, or salts, for instance boehmite, e.g. pseudo- or microcrystalline boehmite, bayerite, amorphous oxide or hydroxide, metal aluminate, or aluminium molybdate.

An important aspect of the invention resides in the presence of this aluminium-containing compound in the final product. The amount of aluminium-containing compound in these compositions can range from 1 to 50 wt%, and is preferably between 5 and 50 wt%. The aluminium-containing compound may serve as a binder, create porosity and a high surface area, and introduce acidic sites. The resulting compositions can, therefore, advantageously be used as absorbents or as catalyst additives or supports.

The aluminium-containing compound may be crystalline or amorphous, and have a high ($>50 \text{ m}^2$) or low ($<50 \text{ m}^2$) surface area, depending on the preparation conditions. For instance, ageing at hydrothermal conditions with intermediate addition of base to increase the pH can result in compositions comprising CLM and microcrystalline boehmite; whereas ageing at lower

temperatures and pressures can result in compositions comprising CLM and quasi-crystalline boehmite, i.e. pseudo-boehmite.

- With the present process it is also possible to prepare compositions comprising
- 5 CLM and divalent metal compound (such as oxide or hydroxide) either by starting with an excess of divalent metal source, or by leaching out some of the divalent metal from the calcined product during ageing. Examples of such compositions are compositions of CLM and ZnO, compositions of CLM and Zn(OH)₂, and compositions of CLM, ZnO, and (pseudo)boehmite.
- 10 Furthermore, compositions comprising CLM and transition metal compounds can be formed by using an excess of ammonium transition metal salt.

- The CLMs or CLM-containing compositions prepared according to the process of the present invention may optionally be shaped to form shaped bodies. This
- 15 shaping can be conducted either after or during the preparation of the CLM or the CLM-containing composition. For instance, the slurry of water-insoluble aluminium source and divalent metal source of step a) can be shaped before performing calcination step b), the anionic clay formed in step c) can be shaped before calcination, or the material can be shaped during ageing step e) by
- 20 performing this step in a kneader which might be heated.

- Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the slurry used for shaping should be adapted to the specific
- 25 shaping step to be conducted. It might be advisable to (partially) remove the liquid used in the slurry and/or add an additional or another liquid, and/or change the pH of the precursor mixture to make the slurry gellable and thus suitable for shaping. Various additives commonly used in the various shaping methods, such as extrusion additives, may be added to the precursor mixture
- 30 used for shaping. During this shaping step other components may be added to

the slurry such as zeolites, clays, silicas, aluminas, phosphates, and other catalytically active materials known in the art.

For some applications it is desirable to have additives present in and/or on the CLMs or CLM-containing compositions. Suitable additives comprise oxides, hydroxides, borates, zirconiates, aluminates, sulfides, carbonates, nitrates, phosphates, silicates, titanates, and halides of rare earth metals (for instance Ce, La), Si, P, B, Group VI, Group VIII, alkaline earth metals (for instance Mg, Ca and Ba), and transition metals (for example W, V, Mn, Fe, Ti, Zr, Cu, Co, Ni, Zn, Mo, Sn).

Said additives can easily be deposited on the CLMs or CLM-containing compositions or they can be added during the process in any of the steps. The additives can for instance be added to the starting compounds, but can also be added separately in any of the slurries used in the process. Alternatively, the additives can be added just before the first or the second calcination step. Preferably, the slurry comprising the additive is milled.

If desired, the CLMs prepared by the process according to the invention or the CLM-containing compositions may be subjected to ion-exchange. Upon ion-exchange the interlayer charge-balancing cations, i.e. NH_4^+ , are replaced with other cations. Examples of suitable cations are Na^+ , K^+ , Al^{3+} , Ni^{2+} , Cu^{2+} , Fe^{2+} , Co^{2+} , Zn^{2+} , other transition metals, alkaline earth and rare earth metals, and pillaring cations such as $[\text{Al}_{13}]^{7+}$ Keggin ions. Said ion-exchange can be conducted before or after drying the CLM or CLM-containing composition.

25

The present invention is further directed to catalyst compositions comprising CLMs prepared by the present process and CLM-containing compositions *per se*. Said catalyst compositions may comprise all components usually present in catalyst compositions, such as matrix and/or binder material, zeolites (e.g. faujasite, pentasil, and beta zeolites), additive components, and additional

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phases like metal oxides, sulfides, nitrides, phosphates, silica, alumina, (swellable) clay, anionic clays, preovskites, titania, titania-alumina, zirconia, spinels, and silica-alumina. For specific purposes, the CLM may be pretreated, e.g. sulfided or nitrified.

- 5 These catalyst compositions can be prepared, for instance, by adding the other catalyst components to the CLMs or CLM-containing compositions before shaping them to form shaped bodies. Alternatively, the catalyst components can be mixed in a slurry with already formed (and subsequently milled) shaped bodies of CLMs or CLM-containing compositions. The resulting mixture can
10 then be shaped again.

The CLMs and CLM-containing compositions can be incorporated into the catalyst composition as such or as shaped bodies. Said catalyst compositions can be used for hydrocarbon conversion and purification, such as catalytic cracking, dehydrogenation, hydrocracking, hydrogenation, hydro-
15 denitrogenation, hydrodesulfurisation, Fisher-Tropsch, sulfur removal from diesel or gasoline, polymerisation, steam reforming, base-catalysed reactions, SO_x and NO_x reduction from auto exhausts or from stationary sources (e.g. FCC units).

- 20 The CLMs prepared by the present process and the CLM-containing compositions according to the present invention can also be combined with catalysts as additive compositions, both as such and as shaped bodies. Therefore, the present invention is also directed to catalyst additive compositions comprising CLM. The compositions according to the invention are
25 suitable in FCC processes as active components for SO_x or NO_x removal, metal traps, and reduction of the N and S content in gasoline and diesel fuels, especially when metals such as Ce and/or V are present in or on the CLM.

The CLMs and CLM-containing compositions can be further calcined to form metal oxide compositions. Such a calcination can be performed at temperatures of 200°-1,000°C, preferably 400-600°C, and more preferably close to 450°C.

5 The metal oxide composition can be reduced by hydrogen, CO, or other reducing agents, sulfided, nitrided or otherwise treated to create an active catalyst composition which can suitably be used as a catalyst or catalyst additive for FCC, HPC, dehydrogenation, and Fisher-Tropsch processes. Sulfiding, for instance, is performed by contacting the metal oxide with a sulfur bearing compound, e.g. H₂S. The sulfur bearing compound can be passed over
10 the metal oxide composition as a gas, or it can be present in a slurry comprising the metal-oxide composition.

Alternatively, the metal oxide composition can be rehydrated in aqueous solution and optionally in the presence of additives to form a CLM or CLM-containing composition, optionally containing an additive.

15

The present invention is illustrated by the following examples.

EXAMPLES

Example 1

A mixture of 5 g gibbsite and basic zinc carbonate, $\text{ZnCO}_3 \cdot 2\text{ZnO} \cdot \text{H}_2\text{O}$, (Zn/Al atomic ratio of 3:1) was slurried in 20 ml of water. The slurry was milled. The resulting slurry was dried and subsequently calcined at 500°C for 4 hours. The material was then heated to 85°C and aged overnight, while stirring in an aqueous solution (50 ml) of 0.3 M ammonium heptamolybdate. The product was filtered and washed. According to the powder X-ray diffraction pattern, the product was structurally identical to that reported by M.P. Astier et al.

Example 2

Zn-doped pseudoboehmite was prepared by treating flash calcined gibbsite for 2 hours in an aqueous solution of zinc nitrate (10 wt.% Zn^{2+}) at 120°C, pH 4 (pH adjustment with HNO_3). The solids content of the slurry was 20 wt%. This Zn-doped pseudoboehmite (5 g) was then mixed with basic zinc carbonate (sufficient for reaching a Zn/Al atomic ratio of 2), slurried in water, and milled. The slurry was dried and subsequently calcined at 500°C for 4 hours. The product was aged overnight, while stirring in a solution of ammonium heptamolybdate at 85°C. The resulting material was filtered, washed, and dried at 85°C overnight. According to the powder X-ray diffraction pattern, the product was structurally identical to that reported by M.P. Astier et al.

Example 3

A mixture of 5 g gibbsite, basic nickel carbonate, and zinc hydroxy carbonate was slurried in 20 ml of water. The ration (Zn+Ni):Al was 3:1, whereas the Ni:Zn ratio was 1:1. The slurry was milled. The resulting slurry was dried and subsequently calcined at 500°C for 4 hours. The material was then heated to 85°C and aged overnight, while stirring in an aqueous solution (50 ml) of 0.3 M ammonium heptamolybdate. The product was filtered and washed. According to

the powder X-ray diffraction pattern, the product was structurally identical to that reported by M.P. Astier et al.

Example 4

- 5 A mixture of 5 g gibbsite and basic zinc carbonate (Zn:Al ratio of 3:1) was slurried in 20 ml of water. The slurry was milled. The resulting slurry was dried and subsequently calcined at 500°C for 4 hours. After calcination, the product was rehydrated in a 1M Na₂CO₃ solution at 65°C for 8 hours to obtain a Zn-Al anionic clay. This anionic clay was calcined at 400°C for 4 hours.
- 10 The calcined anionic clay was then heated to 85°C and aged overnight, while stirring in an aqueous solution (50 ml) of 0.3 M ammonium heptamolybdate. The product was filtered and washed. According to the powder X-ray diffraction pattern, the product was structurally identical to that reported by M.P. Astier et al.

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Example 5

- A mixture of 3 g flash calcined gibbsite (Alcoa CP® alumina) and 11.8 g basic zinc carbonate was slurried in water and subsequently calcined at 300°C for 4 hours in air in a muffle furnace. Of the resulting product, 1 g was rehydrated in
- 20 50 ml 1M sodium carbonate at 70°C for 3 days while stirring. The PXRD pattern confirmed the formation of a Zn-Al anionic clay with a small amount of ZnO. The so-prepared Zn-Al anionic clay was calcined at 500°C for 3 hours in air. 5.04 g MoO₃ were added to 50 ml M NH₄OH. The mixture was heated and then mixed with the calcined Zn-Al anionic clay. The resulting slurry was left while
- 25 stirring for 3 days at room temperature and was subsequently filtered, washed with de-ionised water, and dried overnight at 90°C. According to the powder X-ray diffraction pattern, the product was structurally identical to that reported by M.P. Astier et al.

CLAIMS

1. Process for the preparation of a cationic layered material from an aluminium source and a divalent metal source, comprising the steps of:
 - 5 a) preparing a slurry comprising a water-insoluble aluminium source and a divalent metal source,
 - b) drying the slurry and calcining the dried material to form a first calcined material,
 - c) optionally rehydrating the product of step b) to obtain an anionic clay,
 - 10 followed by calcining the anionic clay to form a second calcined material,
 - d) contacting a slurry of either the first or the second calcined material with an ammonium transition metal salt, and
 - e) ageing the resulting slurry.
- 15 2. A process according to claim 1 wherein the product of step b) is rehydrated to obtain an anionic clay, followed by calcining the anionic clay.
3. A process according to claim 1 or 2 wherein the slurry of step a) is aged before conducting step b).
- 20 4. A process according to any one of the preceding claims wherein the product of step e) is filtered and washed.
5. A process according to any one of the preceding claims wherein in step b) the dried slurry is shaped before calcination.
- 25 6. A process according to claim 2 wherein the anionic clay obtained in step c) is shaped before calcination.

7. A process according to any one of the preceding claims wherein the water-insoluble aluminium source is selected from alumina gel, boehmite, pseudoboehmite, aluminium trihydrate, thermally treated forms of aluminium trihydrate, and mixtures thereof.
- 5
8. A process according to any one of the preceding claims wherein the water-insoluble aluminium source is doped with at least one metal compound.
9. A process according to any one of the preceding claims wherein the divalent metal is an oxide, hydroxide, hydroxycarbonate, or carbonate of Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} or Cu^{2+} , or a combination thereof.
- 10
10. A process according to any one of the preceding claims wherein the ammonium transition metal salt is ammonium heptamolybdate, ammonium tungstate, ammonium vanadate or ammonium dichromate, or a combination thereof.
- 15
11. A process according to any one of the preceding claims wherein the product of step e) is dried and the resulting dried product is calcined at 200-1,000°C.
- 20
12. A process according to claim 11 wherein the calcined product is rehydrated in the presence of an additive.
13. Composition comprising a cationic layered material and 1-50 weight percent of aluminium oxide, aluminium hydroxide, or aluminium salt.
- 25
14. A composition according to claim 13 wherein the aluminium oxide or hydroxide is boehmite, pseudoboehmite, or bayerite.

15. A composition according to claim 13 or 14 wherein the aluminium oxide or hydroxide is doped with rare earth metals or transition metals.
- 5 16. Composition comprising a cationic layered material and a divalent metal compound.
17. Composition comprising a cationic layered material and an ammonium transition metal compound.
- 10 18. Shaped body comprising a cationic layered material obtainable by the process according to claim 5 or 6.
19. Shaped body comprising a composition according to any one of claims 13-17.
- 15 20. FCC catalyst composition comprising a composition according to any one of claims 13-17.
- 20 21. FCC catalyst additive composition comprising a composition according to any one of claims 13-17.

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CLAIMS

1. Process for the preparation of a cationic layered material from an aluminium source and a divalent metal source, comprising the steps of:
 - 5 a) preparing a slurry comprising a water-insoluble aluminium source and a divalent metal source,
 - b) drying the slurry and calcining the dried material to form a first calcined material,
 - c) optionally rehydrating the product of step b) to obtain an anionic clay,
10 followed by calcining the anionic clay to form a second calcined material,
 - d) contacting a slurry of either the first or the second calcined material with an ammonium transition metal salt, and
 - e) ageing the resulting slurry.
- 15 2. A process according to claim 1 wherein the product of step b) is rehydrated to obtain an anionic clay, followed by calcining the anionic clay.
3. A process according to claim 1 or 2 wherein the slurry of step a) is aged before conducting step b).
- 20 4. A process according to any one of the preceding claims wherein the product of step e) is filtered and washed.
5. A process according to any one of the preceding claims wherein in step b) the dried slurry is shaped before calcination.
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6. A process according to claim 2 wherein the anionic clay obtained in step c) is shaped before calcination.

7. A process according to any one of the preceding claims wherein the water-insoluble aluminium source is selected from alumina gel, boehmite, pseudoboehmite, aluminium trihydrate, thermally treated forms of aluminium trihydrate, and mixtures thereof.
- 5
8. A process according to any one of the preceding claims wherein the water-insoluble aluminium source is doped with at least one metal compound.
9. A process according to any one of the preceding claims wherein the divalent metal is an oxide, hydroxide, hydroxycarbonate, or carbonate of Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} or Cu^{2+} , or a combination thereof.
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- 10.A process according to any one of the preceding claims wherein the ammonium transition metal salt is ammonium heptamolybdate, ammonium tungstate, ammonium vanadate or ammonium dichromate, or a combination thereof.
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- 11.A process according to any one of the preceding claims wherein the product of step e) is dried and the resulting dried product is calcined at 200-1,000°C.
- 20
- 12.A process according to claim 11 wherein the calcined product is rehydrated in the presence of an additive.
- 13.Composition comprising a cationic layered material and 1-50 weight percent of aluminium oxide, aluminium hydroxide, or aluminium salt.
- 25
- 14.A composition according to claim 13 wherein the aluminium oxide or hydroxide is boehmite, pseudoboehmite, or bayerite.

15. A composition according to claim 13 or 14 wherein the aluminium oxide or hydroxide is doped with rare earth metals or transition metals.
- 5 16. Composition comprising a cationic layered material and a divalent metal compound.
17. Composition comprising a cationic layered material and an ammonium transition metal compound.
- 10 18. Shaped body comprising a cationic layered material obtainable by the process according to claim 5 or 6.
19. Shaped body comprising a composition according to any one of claims 13-17.
- 15 20. FCC catalyst composition comprising a composition according to any one of claims 13-17.
- 20 21. FCC catalyst additive composition comprising a composition according to any one of claims 13-17.

ABSTRACT

The present invention provides a process for the production of cationic layered materials using inexpensive raw materials. In particular, the use of metal salts is avoided. In addition, in one embodiment of this invention the formation of an anionic clay as intermediate is essentially avoided.

The process comprises the following steps:

- a) preparing a slurry comprising a water-insoluble aluminium source and a divalent metal source,
- 10 b) drying the slurry and calcining the dried product to form a first calcined material,
- c) optionally rehydrating the product of step b) to obtain an anionic clay, followed by calcining the anionic clay to form a second calcined material,
- d) contacting a slurry of either the first or the second calcined material with an ammonium transition metal salt, and
- 15 e) ageing the resulting slurry.

ABSTRACT

The present invention provides a process for the production of cationic layered materials using inexpensive raw materials. In particular, the use of metal salts is avoided. In addition, in one embodiment of this invention the formation of an anionic clay as intermediate is essentially avoided.

The process comprises the following steps:

- a) preparing a slurry comprising a water-insoluble aluminium source and a divalent metal source,
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- 15 e) ageing the resulting slurry.

